

# Comparative Raman Studies of $\text{Sr}_2\text{RuO}_4$ , $\text{Sr}_3\text{Ru}_2\text{O}_7$ and $\text{Sr}_4\text{Ru}_3\text{O}_{10}$

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The polarized Raman spectra of layered ruthenates of the  $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$  ( $n = 1, 2, 3$ ) Ruddlesden-Popper series were measured between 10 and 300 K. The phonon spectra of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  and  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  confirmed earlier reports for correlated rotations of neighboring  $\text{RuO}_6$  octahedra within double or triple perovskite blocks. The observed Raman lines of  $A_g$  or  $B_{1g}$  symmetry were assigned to particular atomic vibrations by considering the Raman modes in simplified structures with only one double or triple  $\text{RuO}_6$  layer per unit cell and by comparison to the predictions of lattice dynamical calculations for the real  $P_{\text{ban}}$  and  $P_{\text{bam}}$  structures. Along with discrete phonon lines, a continuum scattering, presumably of electronic origin, is present in the  $zz$ ,  $xx$  and  $xy$ , but not in the  $x'y'$  and  $zx$  spectra. Its interference with phonons results in Fano shape for some of the lines in the  $xx$  and  $xy$  spectra. The temperature dependencies of phonon parameters of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  exhibit no anomaly between 10 and 300 K where no magnetic transition occur. In contrast, two  $B_{1g}$  lines in the spectra of  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ , corresponding to oxygen vibrations modulating the Ru-O-Ru bond angle, show noticeable hardening with ferromagnetic ordering at 105 K, thus indicating strong spin-phonon interaction.

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## I. INTRODUCTION

The properties of layered ruthenates  $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$  ( $n = 1, 2, 3$ ), known as the Ruddlesden-Popper series, exhibit strong dependence on the number of  $\text{RuO}_6$  octahedral layers.  $\text{Sr}_2\text{RuO}_4$  ( $n = 1$ ) is  $p$ -wave superconductor,[1, 2]  $\text{Sr}_3\text{Ru}_2\text{O}_7$  ( $n = 2$ ) is nearly ferromagnetic (enhanced paramagnetic) metal,[3] whereas  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  ( $n = 3$ ,  $T_C = 105$  K) is a ferromagnetic metal.[5, 6] There are indications that the variations with  $n$  of the magnetic and transport properties of  $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$  are partly related to the structural distortions in  $\text{Sr}_3\text{Ru}_2\text{O}_7$  and  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ . While the structure of  $\text{Sr}_2\text{RuO}_4$  is tetragonal ( $I4/mmm$ , No.139, Fig.1) and the Ru-O-Ru angle in the  $ab$  plane is  $180^\circ$ , the structures of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  ( $P_{\text{ban}}$ , No.50) and  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  ( $P_{\text{bam}}$ , No. 55) are orthorhombic due to correlated rotations about the  $c$ -axis of the neighboring corner-sharing octahedra within each layer of the double or triple perovskite blocks.[3, 4, 5, 6] These rotations result in decrease of the Ru-O-Ru angle in the  $ab$  plane to  $166^\circ$  for  $\text{Sr}_3\text{Ru}_2\text{O}_7$  and  $169^\circ$  for the outer layers and  $158^\circ$  for the middle layers of  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ , respectively. The Sr-based ruthenates, however, are less distorted than corresponding Ca-based compounds. Indeed, besides being rotated around the  $c$  axis, the  $\text{RuO}_6$  octahedra in  $\text{Ca}_2\text{RuO}_4$  ( $P_{\text{bca}}$ , No.61)[2] and  $\text{Ca}_3\text{Ru}_2\text{O}_7$  ( $A2_1ma$ , No.36) [7] are also tilted around an axis lying in the  $\text{RuO}_2$  plane.

The coupling among the charge, lattice and spin degrees of freedom in  $(\text{Ca,Sr})_{n+1}\text{Ru}_n\text{O}_{3n+1}$  compounds has been subject of several magnetotransport[3, 6], pressure[8, 9] and Raman[9, 10, 11, 12] studies. The

polarization-, temperature-, pressure- and substitution-dependent Raman spectra allowed observation of the two-magnon scattering, opening of the spin gap, and pressure- and substitution-induced variations in metal-insulator transition in  $\text{Ca}_2\text{RuO}_4$ [9],  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ [12] and  $\text{Ca}_3\text{Ru}_2\text{O}_7$ [9, 10], as well as spin gap and strong direction-dependent electron-phonon interaction in  $\text{Sr}_2\text{RuO}_4$ [11]. The latter studies illustrated the ability of Raman scattering to provide information on the interplay of spin, charge, and lattice degrees of freedom. To our knowledge, there are yet no reports on the Raman spectroscopy of double-layer  $\text{Sr}_3\text{Ru}_2\text{O}_7$  and triple-layer  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ . The Raman spectra of these materials and their variations with temperature are of definite interest as they contain information about the local structure, electron-phonon, spin-phonon interactions and their variations with the number of  $\text{RuO}_6$  layers. An essential precondition for correct analysis and understanding of complex structure-properties relationships is the assignment of the Raman lines to particular atomic motions.

In this work we present results of comparative polarization- and temperature-dependent Raman studies of  $\text{Sr}_2\text{RuO}_4$ ,  $\text{Sr}_3\text{Ru}_2\text{O}_7$  and  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  between 10 and 300 K. The spectra of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  and  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  provide clear evidence for a structure containing correlated rotations of  $\text{RuO}_6$  octahedra within perovskite blocks. On the basis of their symmetry, considering corresponding modes in simplified tetragonal structures, containing  $\text{RuO}_6$  rotations, and by comparison to the predictions of lattice dynamical calculations (LDC) for the real orthorhombic  $P_{\text{ban}}$  and  $P_{\text{bam}}$  structures, the observed Raman lines of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  and  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  are assigned to

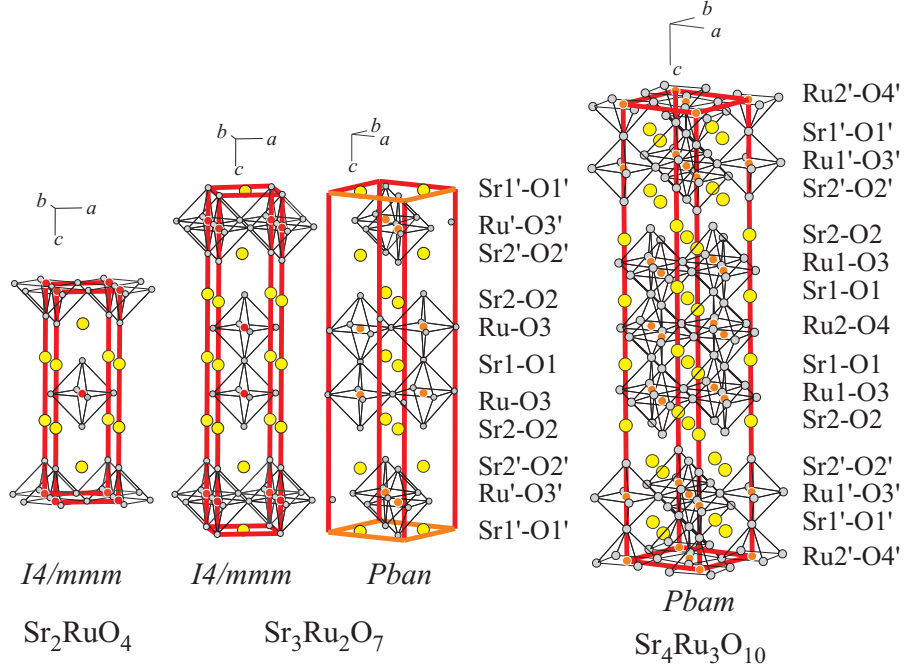


FIG. 1: Units cells of  $\text{Sr}_2\text{RuO}_4$  ( $I4/mmm$ ),  $\text{Sr}_3\text{Ru}_2\text{O}_7$  ( $I4/mmm$  and  $Pban$ ) and  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  ( $Pbam$ ).

definite phonon modes. Except for phonon lines, a continuum scattering, presumably of electronic origin, with components of  $A_g$  ( $xx$  and  $zz$ ) and  $B_{1g}$  ( $xy$ ) symmetry is present in the whole temperature range. Its interference with phonons results in Fano shape for some of the lines in the  $xx$  and  $xy$  spectra. Phonon anomalies related to magnetic ordering at  $T_C = 105$  K are observed in the temperature-dependent spectra of  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ .

## II. SAMPLES, EXPERIMENTAL AND LATTICE DYNAMICAL CALCULATIONS

Rectangular platelet-like single crystals of  $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$  ( $n = 1, 2, 3$ ) with typical size  $1 \times 1 \times 0.2$  mm<sup>3</sup> were grown using  $\text{SrCO}_3$  and  $\text{RuO}_2$  as starting materials and  $\text{SrCl}_2$  as a flux. The compositions  $\text{Sr}_2\text{RuO}_4$ ,  $\text{Sr}_3\text{Ru}_2\text{O}_7$ , and  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  were obtained by varying the  $\text{SrCO}_3$ : $\text{SrCl}_2$  ratio and temperature profiles. The temperature profile was basically as follows: (1) Temperature increase to 1400-1500°C in 7 hours and then constant temperature for 25 hours; (2) Cooling down to 1250-1350°C at a rate of 2 deg/hour; (3) Further cooling to room temperature in 1 hour.

The x-ray diffraction showed that the lattice parameters of all three compounds corresponded to the ones known from the literature. It was also established and further confirmed by Raman polarization selection rules that the large surfaces of the crystal platelets were parallel to the (001) plane and their edges were along either

$\{100\}$  or  $\{110\}$  directions.

Raman spectra were collected using Jobin-Yvon HR640 spectrometer equipped with microscope (100× or 50× objective, focus spot size 1-3 μm), notch filters and liquid-nitrogen-cooled charge-coupled device (CCD) detector. The He-Ne (632.8 nm) and Ar<sup>+</sup> (514.5 nm and 488.0 nm) laser lines were used for excitation. The lack of spurious signals from impurity phases was verified by the reproducibility of the spectra and their strict polarization. Given the crystallographic directions were known, measurements could be done in several exact backward scattering configurations:  $z(xx)\bar{z}$ ,  $z(yy)\bar{z}$ ,  $z(xy)\bar{z}$ ,  $z(x'x')\bar{z}$ ,  $z(x'y')\bar{z}$ ,  $y(zz)\bar{y}$ ,  $y(zx)\bar{y}$ ,  $y(xy)\bar{y}$ ,  $y(x'x')\bar{y}$ . The first and forth letters in these notations stay for the directions of incident and scattered light, whereas their polarizations are denoted by the second and third letters, respectively. As  $x \equiv [100]$  and  $y \equiv [010]$  are indistinguishable,  $x$  and  $y$  are interchangeable. The same is valid for  $x' \equiv [110]$  and  $y' \equiv [\bar{1}\bar{1}0]$ . Further, the short notations  $xx$ ,  $zz$ ,  $x'x'$ ,  $x'y'$  and  $zx$  will also be used.

The lattice dynamical calculations were done using a shell model described in detail in Ref.[13]. This model gives an adequate description of the vibrations in perovskitelike structures because it accounts for their predominant ionicity. The ionic interactions are represented by long-range Coulomb potentials and short-range repulsive potentials of the Born-Mayer form  $ae^{-br}$  where  $a$  and  $b$  are constants and  $r$  is the interionic separation. The deformation of the electron charge density of the ions is described in the dipole approximation considering each

atom as consisting of a point charged core and a concentric spherical massless shell with charge  $Y$ . Each core and its shell are coupled together with a force constant  $k$  giving rise to the free ionic polarizability  $\alpha = Y^2/k$ . The model parameters for the strontium, ruthenium, and oxygen ions and their interaction potentials are taken from a previous study of simpler compounds with perovskitelike structure[13, 14].

### III. RESULTS AND DISCUSSION

#### A. $\text{Sr}_2\text{RuO}_4$

The polarized Raman spectra of  $\text{Sr}_2\text{RuO}_4$  at room temperature as obtained with 488.0 nm excitation are shown in Fig.2. Three of the four ( $2A_{1g} + 2E_g$ ) Raman allowed phonons are observed at  $200 \text{ cm}^{-1}$  ( $A_{1g}$ , Sr vibrations along  $z$ ),  $247 \text{ cm}^{-1}$  ( $E_g$ , apex oxygen vibrations in the  $xy$  plane), and  $545 \text{ cm}^{-1}$  ( $A_{1g}$ , apex oxygen vibrations along  $z$ ), in consistence with earlier reports of Udagawa et al.[15] and Sakita et al.[11]. The Raman phonon intensities  $I_\omega$  exhibit clear resonant behavior. For example in the  $zz$ -polarized spectra the  $I_{545}/I_{200}$  ratio is 19.3 for 632.8 nm (1.96 eV), 4.2 for 514.5 nm (2.41 eV), and 3.5 for 488.0 nm (2.54 eV) excitations, respectively. In the  $xx$  polarized spectra the corresponding values are 2.1, 1.5, and 4.2. For all three excitation energies used, the  $y(xx)\bar{y}$  and  $z(xx)\bar{z}$  spectra were practically identical.

Except for the phonon lines, an electronic background was present in all spectra. The electronic Raman scattering for incident polarization parallel to the  $ab$  plane has previously been reported by Yamanaka et al.[16], who observed structureless continuum with  $A_{1g}$ ,  $B_{1g}$  and  $B_{2g}$  components of comparable intensity. Our measurements have shown, however, that the  $A_{1g}(xx)$  component of the continuum is much weaker than those of  $B_{1g}(x'y')$  and  $B_{2g}(xy)$  symmetry.

#### B. $\text{Sr}_3\text{Ru}_2\text{O}_7$

The orthorhombic  $Pban$  structure of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  can be obtained from the idealized  $I4/mmm$  structure (similar to  $\text{Sr}_2\text{RuO}_4$ , see also Fig.1), by ordered counter-phase rotations of  $\text{RuO}_6$  octahedra around the  $z$ -axis. The  $x$  and  $y$  axes of the  $Pban$  structure are rotated by 45 degree with respect to those of the tetragonal one and the  $a$  and  $b$ -parameters are larger by factor  $\sqrt{2}$ . While ten  $\Gamma$ -point phonon modes ( $4A_{1g} + B_{1g} + 5E_g$ ) are Raman-allowed in the tetragonal  $I4/mmm$  structure of  $\text{Sr}_3\text{Ru}_2\text{O}_7$ , much more modes ( $12A_g + 16B_{1g} + 22B_{2g} + 22B_{3g}$ ) are Raman-allowed in the  $Pban$  structure due to the doubling of unit cell, absence of the cell centering and appearance of new modes related to  $\text{RuO}_6$  rotations. One should not expect, however, observation of such a large number of Raman lines, as to each  $A_{1g}$ ,  $B_{1g}$  or  $E_g$  tetragonal mode one can juxtapose a pair of two  $A_g$ , two  $B_{1g}$  or  $B_{2g} + B_{3g}$

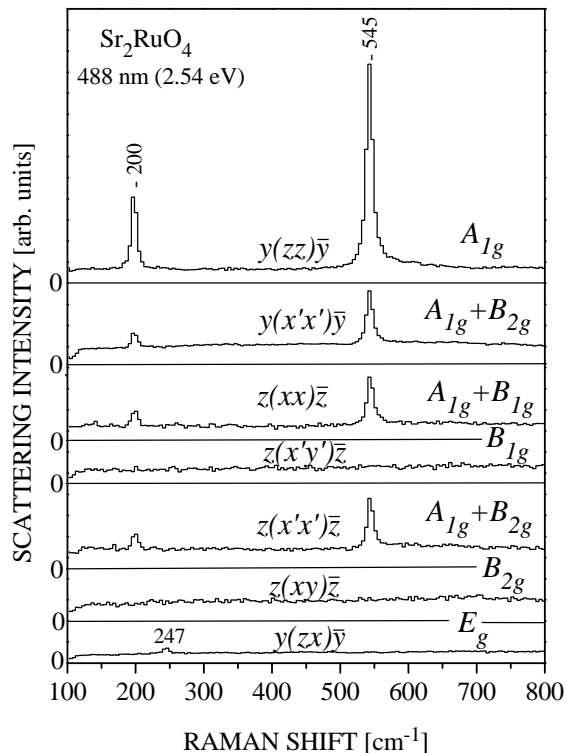


FIG. 2: Polarized Raman spectra of  $\text{Sr}_2\text{RuO}_4$ , obtained at room temperature with 488 nm excitation. A continuum background is present in all spectra.

orthorhombic modes, which involve practically the same atomic vibrations and have very close frequencies (see Table I for LDC of the  $A_g$  and  $B_{1g}$  modes). Experimentally, these pairs will be observed as a single line.

Polarized Raman spectra of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  measured at room temperature with 633 nm, 515 nm and 488 nm laser line excitation are shown in Fig. 3. Five lines of  $A_g$  symmetry are clearly pronounced in the  $xx$  and  $zz$  spectra at 118, 165, 212, 395, and  $577 \text{ cm}^{-1}$ . Another two lines of  $B_{1g}$  symmetry are seen in the  $xy$  spectra at 306 and  $377 \text{ cm}^{-1}$ , but no lines of detectable intensity are observed in the  $zx(z\bar{y})$  spectra where are allowed the modes of  $B_{2g}(B_{3g})$  symmetry. The intensity of the Raman lines changes with excitation energy due to alteration of the resonance conditions. The relative intensities of the  $A_g$  line at  $395 \text{ cm}^{-1}$  and the two  $B_{1g}$  lines, however, remain nearly the same. This suggests that the three modes involve motions of same type of atoms, different from those with main contribution to the  $A_g$  mode at  $577 \text{ cm}^{-1}$ . The number of Raman lines in the spectra of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  is noticeably lower than in the corresponding spectra of  $\text{Ca}_3\text{Ru}_2\text{O}_7$ . [10] This had to be expected as the structure of  $\text{Ca}_3\text{Ru}_2\text{O}_7$  is more strongly distorted and the number of fully symmetrical modes allowed in  $xx$ ,  $yy$  and  $zz$  configurations is higher.

A simple approach to the assignment of the Raman lines is based on the reasonable assumption for weak in-

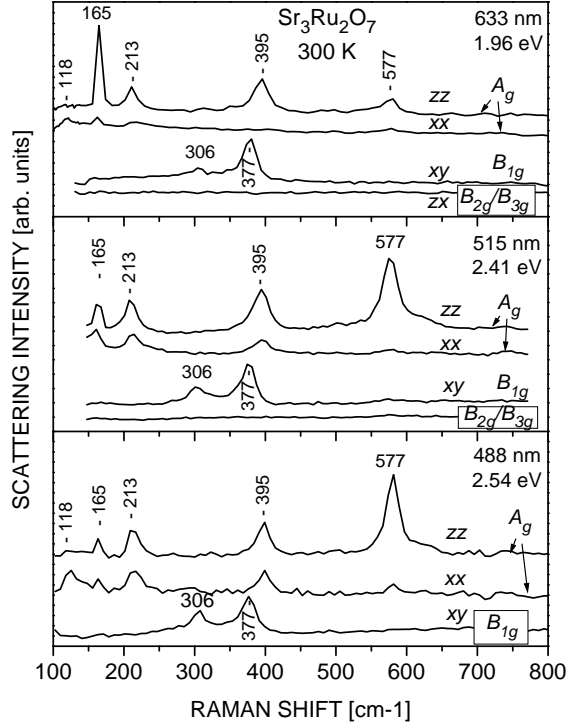


FIG. 3: Polarized Raman spectra of  $\text{Sr}_3\text{Ru}_2\text{O}_7$ , obtained at room temperature with 633 nm, 515 nm, and 488 nm excitation. Some curves are shifted vertically for clarity.

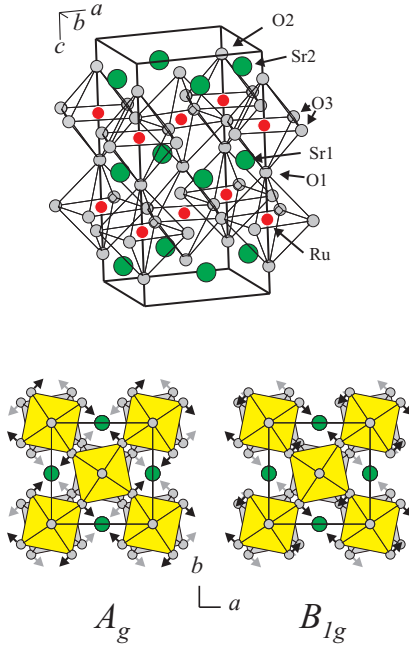


FIG. 4: Simplified distorted structure ( $P4/nbm$ ) of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  with elementary cell containing one double Ru-O layer. The distortion-activated  $A_g$  and  $B_{1g}$  modes are also shown.

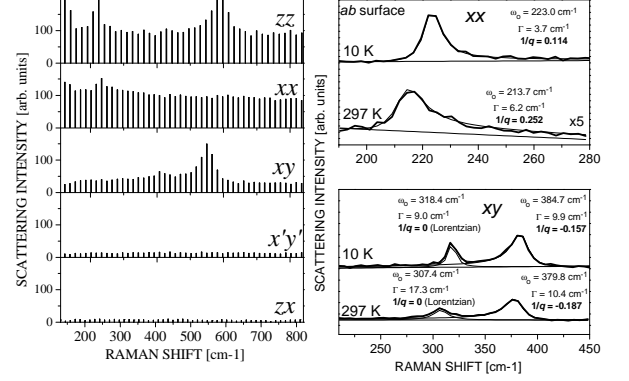


FIG. 5: Left panel: Continuum scattering from  $\text{Sr}_3\text{Ru}_2\text{O}_7$  as obtained with 633 nm excitation for several exact scattering configurations; Right panels: Fano fit of the  $213/223 \text{ cm}^{-1}$   $A_g$  ( $xx$ ) and  $377/384 \text{ cm}^{-1}$   $B_{1g}$  lines. The fit parameters are also given.

interaction between the double Ru-O slabs, the only important distortion being the rotation of the  $\text{RuO}_6$  octahedra. Within such assumption, instead of the real  $Pban$  structure, one can consider a simplified structure with elementary cell containing only one double layer (Fig.4). This structure is tetragonal ( $P4/nbm$ , No.125,  $Z=2$ ) with the same  $a$  and  $b$  parameters as the real one, but twice shorter  $c$  parameter. The normal mode analysis gives  $5A_{1g} + B_{1g} + 4B_{2g} + 11E_g$  Raman modes. Therefore one expects in the  $xx$  and  $zz$  spectra five Raman lines of  $A_g$  symmetry ( $A_{1g}$  in tetragonal notations), which is exactly the case. In the  $xy$  spectra one expects observation of four  $B_{1g}$  modes ( $B_{2g}$  in tetragonal notations), two of them involving mainly oxygen vibrations.

The Raman mode frequencies in ionic materials, such as transition metal oxides, are determined by the mass, charge, and bond lengths of participating atoms as well by the type of atomic motions (stretching, bending or rotational). Based on comparison to other perovskitelike oxides, the modes involving mainly vibration of heavier Ru and Sr or rotational vibrations of oxygens are expected in the frequency range below  $250 \text{ cm}^{-1}$ , the bending oxygen modes - between 200 and  $500 \text{ cm}^{-1}$  and stretching oxygen modes - above  $500 \text{ cm}^{-1}$ . Our LDC for the  $Pban$  structure (Table I) predict that the  $A_g$  modes below  $250 \text{ cm}^{-1}$  are strongly mixed, each involving vibrations along  $z$  of Ru and Sr2 as well as  $\text{RuO}_6$  rotations around  $z$ . In the  $I4/mmm$  structure, however, the rotational motions (see Fig.4), are not Raman active. Therefore, the  $165 \text{ cm}^{-1}$  and  $213 \text{ cm}^{-1}$  lines, which are close to LDC( $Pban$ ) frequency of  $117 \text{ cm}^{-1}$ , which has no partner in the LDC( $I4/mmm$ ) data, is assigned to mainly  $\text{RuO}_6$  rotations. The "soft"-mode temperature

behavior of the latter line is also typical for a rotational mode. As to the two high-frequency  $A_g$  modes, with great certainty, confirmed by LDC, they correspond to out-of-plane in-phase vibrations of O3 ( $395 \text{ cm}^{-1}$ ) and stretching vibrations of O2 ( $577 \text{ cm}^{-1}$ ). The latter frequency is higher than that of the corresponding apex oxygen vibrations in  $\text{Sr}_2\text{RuO}_4$  ( $545 \text{ cm}^{-1}$ ), which can be explained accounting the bond-length changes. Indeed, it is plausible to assume that the force constants  $k_{\text{O-M}}$  between O and the ion M follows the simple  $Z_{\text{O}}Z_{\text{M}}/r_{\text{O-M}}^3$  relation, where  $Z_{\text{O}}$  and  $Z_{\text{M}}$  are the charges of the oxygen and cation, respectively, and  $r_{\text{O-M}}$  is the oxygen-cation bond length. This relation is valid for harmonic ionic crystals and shown to apply for perovskitelike transition metal oxides.[17, 18]. Taking into account that  $\omega^2 = k/m$  and restricting interactions to only nearest-neighbors (Ru and Sr), one obtains for the O2 stretching vibrations

$$\omega^2 \propto Z_{\text{Ru}}/r_{\text{O-Ru}}^3 + Z_{\text{Sr}}/r_{\text{O-Sr}}^3 \quad (1)$$

where  $Z_{\text{Ru}} = 4$ ,  $Z_{\text{Sr}} = 2$ , and the values of  $r_{\text{O-Ru}}$  and  $r_{\text{O-Sr}}$  are respectively  $2.016 \text{ \AA}$  and  $2.459 \text{ \AA}$  for  $\text{Sr}_3\text{Ru}_2\text{O}_7$ [4] and  $2.059 \text{ \AA}$  and  $2.440 \text{ \AA}$  for  $\text{Sr}_2\text{RuO}_4$ [19]. Using these values one obtains  $\omega_{\text{Sr}_3\text{Ru}_2\text{O}_7}/\omega_{\text{Sr}_2\text{RuO}_4} = 1.045$ , which is close to the experimental ratio of 1.059.

There is little doubt too, that the two experimentally observed lines in the  $xy$  spectra correspond to the two oxygen  $B_{2g}$  modes of the distorted  $P4/nbm$  structure. The main atomic motions are out-of-phase vibrations along  $z$  of O3 ( $306 \text{ cm}^{-1}$ ) and "scissors-like" bendings of O3 parallel to the  $xy$  plane ( $377 \text{ cm}^{-1}$ ). The shape of the latter mode is also shown in Fig.4.

Along with the phonon lines, a structureless background of  $A_g(zz \text{ and } xx)$ , and  $B_{1g}(xy)$  symmetry, but not of  $B_{2g}/B_{3g}(zx \text{ or } zy)$  symmetry, is also present in the spectra. This is illustrated in Fig.5 for room temperature spectra taken with  $633 \text{ nm}$  excitation. The observation of relatively strong  $zz$ -polarized continuum was somewhat unexpected as the ARPES measurements[20] and band structure calculations[21] provide evidence for quasi-two-dimensional Fermi-surface sheets, in consistency with reports for large anisotropy of the electrical resistivity ( $\rho_z/\rho_{xy} \approx 40$  at  $300 \text{ K}$ )[3]. The continuum-phonons interference is clearly pronounced only for incident radiation parallel to the  $xy$  plane through Fano shape of the  $213 \text{ cm}^{-1}$   $A_g$  line in the  $xx$  spectra and the  $377 \text{ cm}^{-1}$   $B_{1g}$  line in the  $xy$  spectra (Fig.5). For a phonon coupled to electronic background, the Fano profile  $I(\omega) = I_0(\epsilon + q)^2/(1 + \epsilon^2)$  is generally used to describe the line shape, where  $\epsilon = (\omega - \omega_0)/\Gamma$ ,  $\omega_0$  is the "bare" phonon frequency,  $\Gamma$  is the linewidth, and  $q$  is the asymmetry parameter,  $1/q \propto V$  reflects the electron-phonon interaction  $V$ . While for an uncoupled phonon  $1/q = 0$ , the increase of electron-phonon interaction increases  $|1/q|$ . The values of  $\omega_0$ ,  $\Gamma$ , and  $1/q$  as obtained from the Fano fit of the experimental line profiles are listed in Fig.5.

Fig.6 shows the temperature-dependent  $zz$ ,  $xx$  and  $xy$  Raman spectra of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  between  $10 \text{ K}$  and  $300 \text{ K}$ .

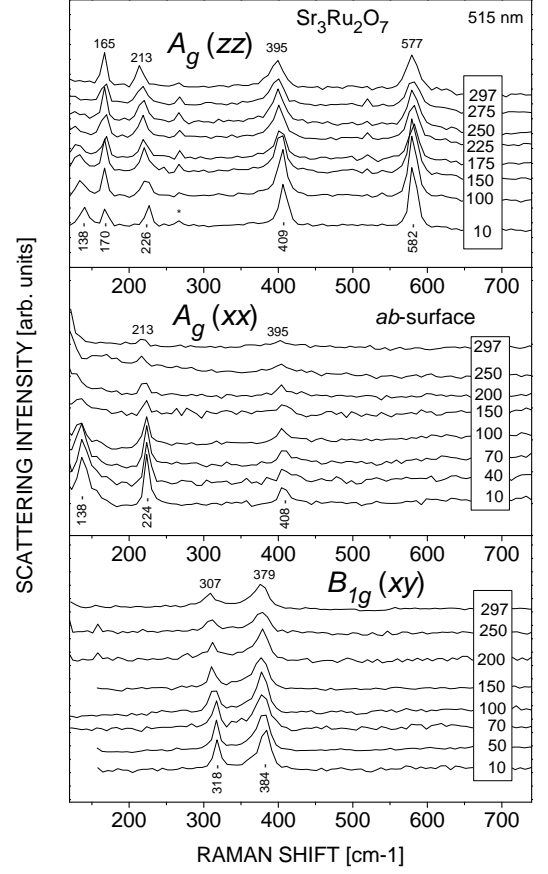


FIG. 6: Temperature-dependent polarized Raman spectra of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  between  $10$  and  $300 \text{ K}$  obtained with  $515 \text{ nm}$  excitation.

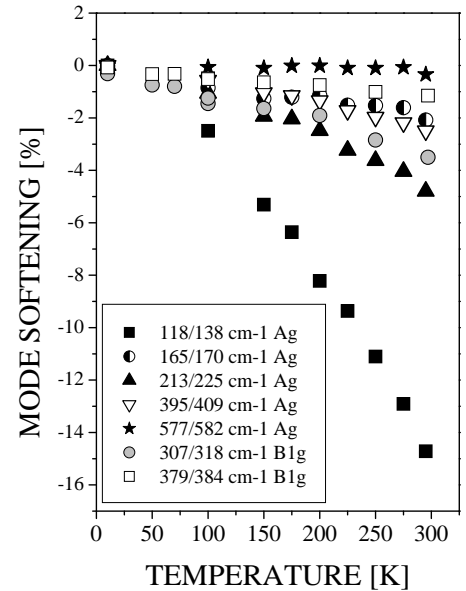


FIG. 7: Variations with  $T$  of the relative changes  $[\omega(T) - \omega(10)]/\omega(10)$  of the  $A_g$  mode frequencies in  $\text{Sr}_3\text{Ru}_2\text{O}_7$ .

TABLE I: Calculated (for the  $Pbam$  and  $I4/mmm$  structures) and experimentally observed  $A_g/A_{1g}$  and  $B_{1g}$  phonon frequencies in  $Sr_3Ru_2O_7$ .

Mode	LDC	Exp	Atomic	Mode	LDC	Mode
$Pbam$	$Pbam$	300K/10K	motions	$I4/mmm$	$P4/nbm$	
$A_g(1)$	117	118/138	RuO <sub>6</sub> rot	$A_{1g}$	180	$A_{1g}$
$A_g(2)$	179	165/170				$A_{1g}$
$A_g(3)$	210	213/225				$A_{1g}$
$A_g(4)$	223	213/225				$A_{1g}$
$A_g(5)$	250		O3(z)	$A_{1g}$	512	$A_{1g}$
$A_g(6)$	254					
$A_g(7)$	402	395/409				
$A_g(8)$	402	395/409				
$A_g(9)$	520		O2(z)	$A_{1g}$	589	$A_{1g}$
$A_g(10)$	522					
$A_g(11)$	580	577/581				
$A_g(12)$	580	577/581				
$B_{1g}(1)$	108					$B_{2g}$
$B_{1g}(2)$	109					
$B_{1g}(3)$	162					
$B_{1g}(4)$	162					
$B_{1g}(5)$	181		O3(z, -z)	$B_{1g}$	310	$B_{2g}$
$B_{1g}(6)$	181					
$B_{1g}(7)$	337	306/316				
$B_{1g}(8)$	337	306/316				
$B_{1g}(9)$	378	377/380	O3(xy)			$B_{2g}$
$B_{1g}(10)$	378	377/380				
$B_{1g}(11)$	466					
$B_{1g}(12)$	466					
$B_{1g}(13)$	521					
$B_{1g}(14)$	521					
$B_{1g}(15)$	726					
$B_{1g}(16)$	726					

The variations of phonon frequencies and line widths with temperature exhibit no anomalies. The relative changes of frequency for all observable modes are summarized in Fig.7. The low frequency  $A_g$  mode shows "soft"-mode behavior, its frequency decreasing by  $\approx 15\%$  between 10 and 300 K, while the frequency of the highest mode remains practically unchanged. The continuum scattering in the  $zz$ ,  $xx$  and  $xy$  spectra only slightly decreases with lowering temperature, in contrast to the case of  $Ca_3Ru_2O_7$ , where a rapid suppression of the electronic background of  $B_{1g}$  symmetry has been observed below the metal-insulator transition at  $T_{MI} \approx 48$  K.[10] The interaction between the continuum and phonons also decreases with lowering temperature, as evidenced from Fig.5, where are compared the  $1/q$  values at 10 and 300 K.

### C. $Sr_4Ru_3O_{10}$

The structure of  $Sr_4Ru_3O_{10}$  has been refined as  $Pbam$ . [5] From symmetry considerations in total 96 ( $20A_g + 20B_{1g} + 28B_{2g} + 28B_{3g}$ ) modes are Raman allowed. Like in the case of  $Sr_3Ru_2O_7$ , however, most modes are practically degenerated in pairs and lower

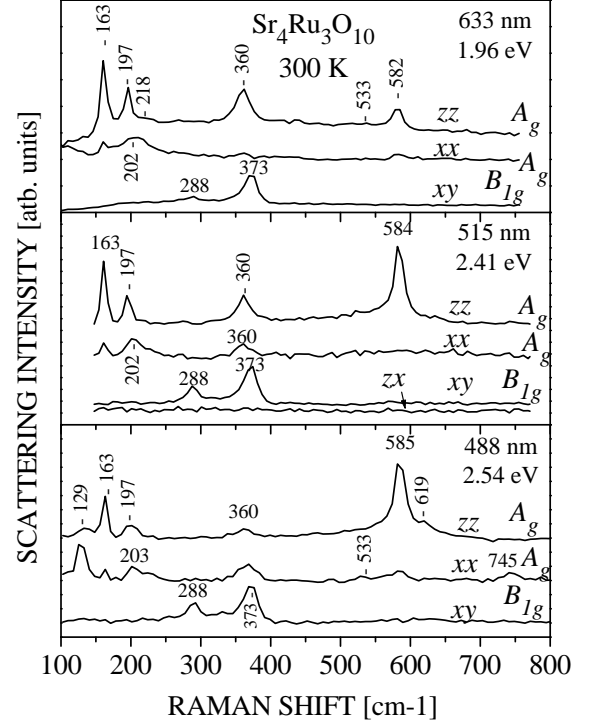


FIG. 8: Polarized Raman spectra of  $Sr_4Ru_3O_{10}$ , obtained at room temperature with 633 nm, 515 nm, and 488 nm excitation. Some curves are shifted vertically for clarity.

number of Raman lines is expected in the spectra. Fig.8 shows the  $zz$ ,  $xx$ ,  $xy$  and  $zx$  spectra obtained at room temperature with 633 nm, 515 nm, and 488 nm excitation. The temperature variations of the spectra between 10 and 300 K are given in Fig.9. Except for line shifts and appearance of additional weak lines, the spectral profiles and their dependence on scattering configuration and excitation wavelength resembles that of  $Sr_3Ru_2O_7$ . Lines of  $A_g$  symmetry are observed at room temperature 129, 163, 195-203, 360-365, 533, 582-585, 619 and 745  $cm^{-1}$ . The broad structure near 200  $cm^{-1}$  in the  $xx$  spectra appears to be a superposition of two lines. This becomes evident at low temperatures where these two line are well separated. Like in the case of  $Sr_3Ru_2O_7$ , only two lines of  $B_{1g}$  symmetry are pronounced and the intensity of the  $B_{2g}$  and  $B_{3g}$  lines is below the detection limit.

To assign the Raman lines to particular phonon modes let us again consider the Raman modes in a simplified distorted tetragonal structure and compare the experimental frequencies to the prediction of lattice dynamical calculations for the real  $Pbam$  structure of  $Sr_4Ru_3O_{10}$ . The simplified structure  $P4/nbm$  (No.127, Z=2), shown in Fig.10, has only one triple layer in the unit cell. It is characterized by the same equal  $a$  and  $b$  parameters as the real structure, but twice shorter  $c$  parameter. From symmetry considerations  $8A_{1g} + 2B_{1g} + 5B_{2g} + 14E_g$  modes are Raman active. The  $A_{1g}$  modes, allowed in  $xx$  and  $zz$  spectra, correspond to  $A_g$  modes in orthorhombic

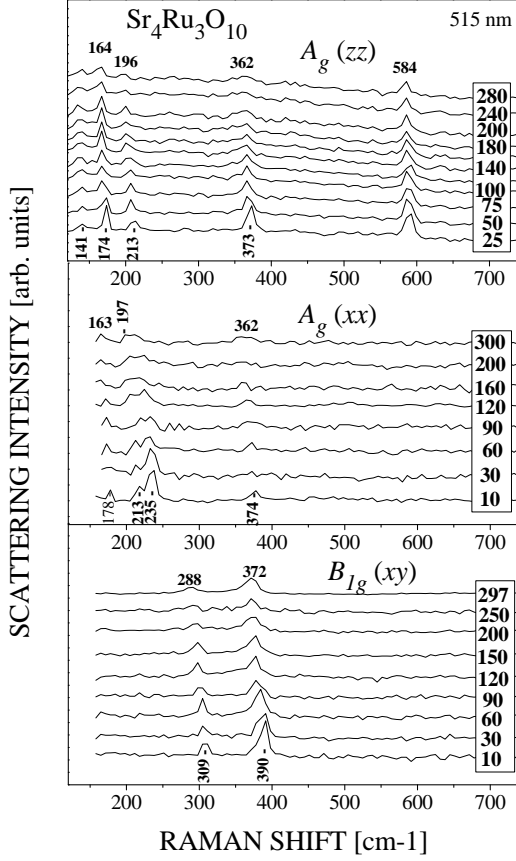


FIG. 9: Variation with T of the  $zz$ ,  $xx$  and  $xy$  spectra of  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ .

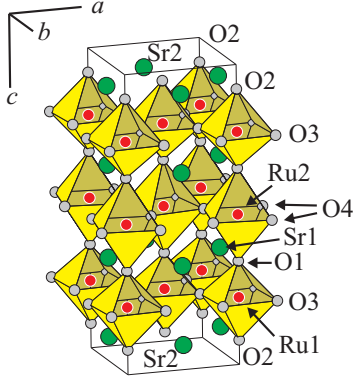


FIG. 10: Simplified distorted structure of  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ :  $P4/mbm$ , No.127,  $Z=2$ .

$Pbam$ , whereas the tetragonal  $B_{2g}$  modes, allowed in the  $xy$  spectra, correspond to the orthorhombic  $B_{1g}$  modes. Compared to the simplified structure of  $\text{Sr}_3\text{Ru}_2\text{O}_7$ , there are three new  $A_{1g}(A_g)$  modes corresponding to: (i) Rotations of middle  $\text{RuO}_6$  octahedra; (ii) Vibrations along  $z$  of internal apex oxygen atoms (O1); (iii) Vibrations along  $z$  of internal Sr1 atoms. The LDC predict close frequen-

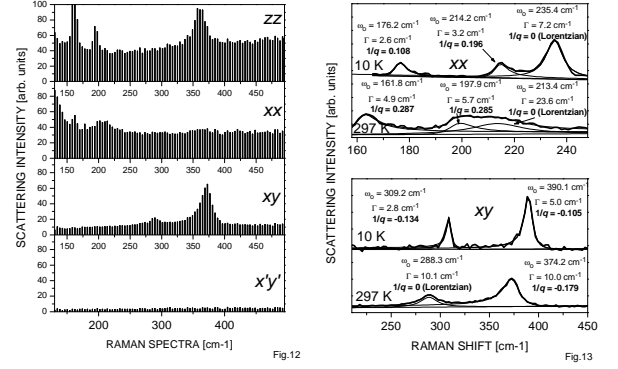


FIG. 11: Left panel: Continuum scattering in the spectra of  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  obtained with 633 nm excitation; Right panels: Fano fits  $xx(A_g)$  and  $xy(B_{1g})$  spectra of  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  obtained with 515 nm excitation at 10 K and 300 K. The fit parameters are also given.

cies for the rotational and Sr1 modes and our assignment of the new  $xx$  polarized  $A_g$  line, seen at low temperature at  $235 \text{ cm}^{-1}$  and also having a "soft"-mode temperature behavior, to rotational vibrations of middle  $\text{RuO}_6$  octahedra is only tentative. There is little doubt that the new  $A_g$  lines at  $745 \text{ cm}^{-1}$ , seen in the  $xx$  spectra with 488 nm excitation, correspond to the vibrations along  $z$  of the inner O1 atoms. Using Eq.(1) with the experimental values of  $r_{O1-Ru2} = 1.991 \text{ \AA}$ ,  $r_{O1-Ru1} = 2.014 \text{ \AA}$  and  $r_{O2-Ru1} = 2.077 \text{ \AA}$ ,  $r_{O2-Sr2'} = 2.380 \text{ \AA}$  one obtains frequency of O1 vibrations along  $z$  should be by factor 1.35 higher than that of the outer apex oxygens (O2). This is in good agreement with the experimentally observed ratio of  $745:584 = 1.28$ . A comparison of phonon frequencies predicted by LDC with experimental data is given in Table II.

The left panel of Fig.11 illustrates the presence in the  $zz$ ,  $xx$  and  $xy$  spectra of  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  of scattering continuum. Like in the case of  $\text{Sr}_3\text{Ru}_2\text{O}_7$ , some lines exhibit clear Fano shape for light polarization parallel to the  $ab$  plane. This is shown in more detail in the right panels of Fig.11.

The ferromagnetic ordering at  $T=105 \text{ K}$  has a moderate, but clearly pronounced effect on phonon parameters and electron-phonon interaction. The temperature dependencies of the position (Fig.12a) and width (Fig.12b) of the Fano shaped  $B_{1g}$  line, corresponding to O3 vibrations in the  $xy$  plane, change their slope near  $T_C$ . The changes of  $1/q(T) \propto V(T)$  (Fig.12c) are even more pronounced, providing evidence that the electron-phonon coupling decreases in the ferromagnetic phase. Weaker changes near  $T_C$  of the parameters of the second  $B_{1g}$  line, corresponding to O3 vibrations in  $z$  direction, are also observed (Figs.12d and 12e).

The magnetic ordering may affect phonon frequency through different mechanisms: exchange stric-



TABLE II: Calculated and experimentally observed  $A_{1g}$  and  $B_{1g}$  phonon frequencies in  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ . The corresponding modes in the simplified  $P4/mbm$  structure are also given.

Mode <i>Pbam</i>	LDC <i>Pbam</i>	Exp 300K/10K	Atomic motions	Mode <i>P4/mbm</i>	Mode <i>Pbam</i>	LDC <i>Pbam</i>	Exp 300K/10K	Atomic motions	Mode <i>P4/mbm</i>
$A_g^{(1)}$	90	129/140	outer $\text{RuO}_6$ rot in $xy$	$A_{1g}$	$B_{1g}^{(1)}$	147			
$A_g^{(2)}$	150	163/178	$\text{Ru1}(z)\text{Sr2}(z)$	$A_{1g}$	$B_{1g}^{(2)}$	151			
$A_g^{(3)}$	173				$B_{1g}^{(3)}$	175			$B_{2g}$
$A_g^{(4)}$	190	198/214	$\text{Sr2}(z)\text{Ru1}(z)$	$A_{1g}$	$B_{1g}^{(4)}$	176			
$A_g^{(5)}$	198				$B_{1g}^{(5)}$	185			$B_{2g}$
$A_g^{(6)}$	210				$B_{1g}^{(6)}$	188			
$A_g^{(7)}$	231	213/235	middle $\text{RuO}_6$ rot in $xy$	$A_{1g}$	$B_{1g}^{(7)}$	327	288/307	$\text{O3}(z, -z)$	$B_{2g}$
$A_g^{(8)}$	234				$B_{1g}^{(8)}$	327			
$A_g^{(9)}$	286				$B_{1g}^{(9)}$	354	373/388	$\text{O3}(xy)$	$B_{2g}$
$A_g^{(10)}$	288				$B_{1g}^{(10)}$	356			
$A_g^{(11)}$	309				$B_{1g}^{(11)}$	464			$B_{2g}$
$A_g^{(12)}$	313				$B_{1g}^{(12)}$	464			
$A_g^{(13)}$	358	361/372	$\text{O3}(z)$	$A_{1g}$	$B_{1g}^{(13)}$	476			
$A_g^{(14)}$	364				$B_{1g}^{(14)}$	476			
$A_g^{(15)}$	512	533/	$\text{O3}(xy)$	$A_{1g}$	$B_{1g}^{(15)}$	482			
$A_g^{(16)}$	514				$B_{1g}^{(16)}$	482			
$A_g^{(17)}$	552	584/588	$\text{O2}(z)$	$A_{1g}$	$B_{1g}^{(17)}$	708			
$A_g^{(18)}$	562				$B_{1g}^{(18)}$	708			
$A_g^{(19)}$	678	745/	$\text{O1}(z)$	$A_{1g}$					
$A_g^{(20)}$	678								

tion, [15, 22] dependence of the spin energy on ion displacements[22, 23, 24], variations of the density of itinerant carriers near  $T_M$ . [14] Although consistent with observation of anomaly in  $1/q$ , the latter mechanism, proposed to explain the anomalous hardening near  $T_C$  of several Raman modes in ferromagnetic  $\text{SrRuO}_3$ , is irrespective to the bond lengths and band angles being modulated and seems to be of less importance in  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ . The observation of detectable anomaly near  $T_C$  only for modes, which modulate the  $\text{Ru1-O3-Ru1}$  angle, rather favors direct interaction of these phonons with the magnetization.[22, 24].

#### IV. CONCLUSIONS

We studied in detail the polarized Raman spectra of  $\text{Sr}_2\text{RuO}_4$ ,  $\text{Sr}_3\text{Ru}_2\text{O}_7$  and  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  with particular attention to the two latter compounds as their phonon spectra have not been reported so far. All observed Raman lines are of either  $A_g$  or  $B_{1g}$  symmetry. They have been assigned to definite atomic vibrations by: (1) considering the Raman active modes in simplified tetragonal  $P4/nbm$  and  $P4/mbm$  structures, which contain only one double or triple  $\text{RuO}_6$  layers per unit cell and account for the rotational distortions; (2) comparison to the

predictions of lattice dynamical calculations for the real orthorhombic double layer  $Pbna$  and triple layer  $Pbam$  structures. Except for the discrete phonon lines, a continuum background, presumably of electronic origin, is present in the  $zz$ ,  $xx$  and  $xy$ , but not in the  $x'y'$  and  $zx$  spectra. The interaction of  $xx$  and  $xy$  continuum with the modes involving atomic motions in the  $ab$  plane results in Fano shape of corresponding Raman lines. While no anomaly in phonon parameters of  $\text{Sr}_3\text{Ru}_2\text{O}_7$  is seen between 10 and 300 K, where no magnetic transition occur, an anomaly is observed near ferromagnetic transition at 105 K in  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ .

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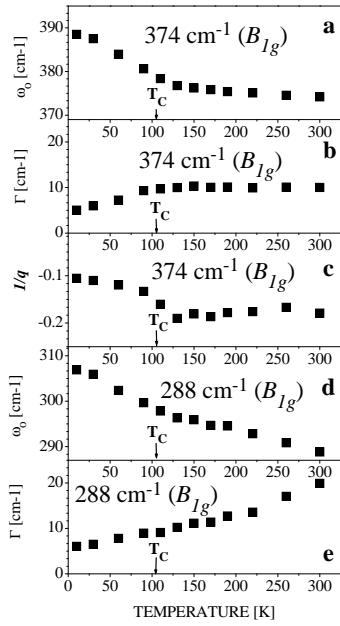


FIG. 12: Variations with  $T$  of (a):  $\omega_0$ , (b):  $\Gamma$ , and (c):  $1/q \sim V$  for the Fano shaped  $B_{1g}$  line at 374/389  $\text{cm}^{-1}$ . No anomaly near  $T_C$  is observed, however, for the position (d) and the width (e) of the Lorentzian  $B_{1g}$  line at 288/308  $\text{cm}^{-1}$ .

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